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(54) **GAS GENERATING AGENT FOR AIR BAGS.**

(57) A gas generating agent for air bags which consists of a nitrogen-containing organic compound and an oxohalogenate, has a high impact ignitability, a high combustion rate and a high gas generation rate, and can attain a comparatively low combustion temperature.

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Technical Field

This invention relates to an air bag gas generating composition.

5 Background Art

The so-called air bag system in which a nylon bag stowed in the steering wheel assembly or dashboard of a car is inflated on sensing a car crash occurring at high speed to thereby protect the driver and other passengers against being injured or killed by the impact against the steering wheel or front glass is claiming a phenomenally increasing share of the market reflecting the current rigorous requirements concerning driving safety.

In this air bag system, a gas generating composition is ignited, either electrically or mechanically, in an instant on sensing a car crash to thereby inflate the bag with the gas so generated. The gas generating composition is generally supplied as molded into a pellet or disk form. It is essential that such a gas generating composition insures an appropriate burning velocity. If the burning velocity is too low, the bag cannot be inflated in an instant so that the system fails to achieve its object. The gas generating composition is a powdery composition having the property to get ignited by a shock. Shock ignitability is the sensitivity of a powder to shock ignition and an excessively high shock sensitivity is undesirable from the standpoint of safety because it represents a high risk of explosion in the course of production, e.g. in the mixing stage or in the molding stage. Therefore, shock sensitivity is preferably as low as possible.

It is also necessary that the combustion temperature of the gas generating composition be not too high. This is because, to absorb the shock of a car crash to the driver or passenger and help him to escape, generally the inflated air bag then releases the internal gas to shrink but if the combustion temperature is too high, the released gas is also hot enough to cause the passenger to sustain a burn, perforate the bag to detract from its function, or burn the bag to induce a car fire.

The known air bag gas generating compositions comprise sodium azide as the gas generating base and certain additives such as an oxidizing agent [e.g. metal oxides such as TiO_2 , MnO_2 , Fe_2O_3 , CuO , etc., nitrates such as NaNO_3 , KNO_3 , $\text{Cu}(\text{NO}_3)_2$, etc., perchlorates such as KClO_4 , NaClO_4 , etc. and chlorates such as KClO_3 , NaClO_3 , etc.], a reducing metal [Zr, Mg, Al, Ti, etc.], a cooling agent [Na_2CO_3 , K_2CO_3 , CaCO_3 , FeSO_4 , etc.], a pH control agent [iron sulfate etc.], a mechanical performance agent [MoS_2 , KBr, graphite, etc.] and so on.

Such sodium azide-based gas generating compositions are in common use today partly because the generated gas is nitrogen gas for the most part and partly because they have adequate burning velocities and relatively low combustion temperatures. However, sodium azide has the following disadvantages.

(1) It has a risk for causing a fire on decomposition or combustion. Thus, since a fire may be induced in the course of production (on mixing with the oxidising agent, in the final granulation stage, etc.), it requires a rigorous safety control.

(2) It produces Na on decomposition. Since Na reacts with water to generate hydrogen and become ignited to produce a toxic fume, there is considerable difficulty in treatment.

(3) It reacts with the oxidizing agent to liberate toxic substances such as Na_2O and its derivatives (such as NaOH), thus calling for careful handling in the course of production.

(4) It is acknowledged that the gas generated on combustion or decomposition of sodium azide is rich in nitrogen and very lean in toxic substances so that there is practically no problem. However, for added safety, a further reduction in the level of toxic substances is desirable.

(5) Crude sodium azide in gas generating compositions is hygroscopic and since the absorption of moisture leads to a decrease in combustibility, there must be an effective provision for the prevention of moisture absorption.

(6) Since it is a toxic and hazardous substance, an additional capital investment is needed for securing safety.

In view of the above disadvantages of sodium azide, the advent has been awaited of an air bag gas generating composition which, compared with the sodium azide-based gas generating composition mentioned above, would have an equivalent or lower shock ignitability, equivalent or higher burning velocity and gas output, and relatively low combustion temperature, and which is lower in the risk of fire and intoxication hazards and lower in costs than the sodium azide-based gas generating composition.

Meanwhile, several attempts have been made to use a nitrogen-containing compound as the base of a gas generating composition. For example, it has been proposed to subject a reducing metal, such as Zr or Mg, and an oxidizing compound, such as potassium perchlorate or potassium chlorate, to redox reaction to thereby ignite the gas generating base with the resultant heat of reaction. As the gas generating base,

smokeless powder, nitrocellulose, azodicarbonamide, aminoguanidine and thiourea have been mentioned (Japanese Examined Patent Publications No. 9734/74 and No. 21171/74). However, the burning velocity that can be obtained by the above method is insufficient for practical application to the air bag. Moreover, since the mixture of reducing metal and oxidising compound has a very high shock sensitivity, the risk of handling hazards is high. Furthermore, the combustion temperature is also suspected to be too high.

Japanese Unexamined Patent Publication No. 118979/75 discloses an air bag gas generating composition comprising a nitrogen-containing compound such as azodicarbonamide, trihydrazinotriazine or the like and an oxidizing agent such as potassium permanganate, manganese dioxide, barium dichromate, barium peroxide or the like. However, the use of potassium permanganate or manganese dioxide as the oxidizing agent does not insure satisfactory shock sensitivity or burning velocity, while the use of barium dichromate or barium peroxide as the oxidizing agent gives rise to toxic substances in the liberated gas.

It is an object of this invention to provide an air bag gas generating composition having a shock sensitivity either equivalent to or lower than that of the gas generating composition based on sodium azide.

Another object of this invention is to provide an air bag gas generating composition which is either equivalent to or even higher than the sodium azide-based gas generating composition in burning velocity and gas output.

A still further object of this invention is to provide an air bag gas generating composition which is free from the above-mentioned disadvantages (1) through (6) of the azide compound.

It is a further object of this invention to provide an air bag gas generating composition which is low in combustion temperature with a lower risk of fire and intoxication hazards as compared with sodium azide.

Disclosure of Invention

The inventor of this invention made an extensive exploration to accomplish the above objects with his attention focused on nitrogen-containing compounds which by themselves have very low risks of fire or intoxication hazards due to decomposition or combustion and found that by causing a nitrogen-containing compound to react directly with a defined oxidizing agent, that is a halogen oxo acid salt, taking advantage of the reducing property of the former instead of combusting the nitrogen-containing compound with the heat of a redox reaction, there can be realized not only a shock sensitivity either equivalent to or lower than that of the sodium azide-based gas generating composition but also a burning velocity and a gas output, both of which are either equivalent to or higher than those of said sodium azide-based composition, as well as a practically useful, low combustion temperature.

This invention is, therefore, directed to an air bag gas generating composition comprising a nitrogen-containing organic compound and a halogen oxo acid salt.

In accordance with this invention a nitrogen-containing compound is used as the gas generation base. There is no particular limitation on the nitrogen-containing compound only if it is an organic compound containing at least one nitrogen atom within its molecule. Thus, for example, amino-containing compounds, nitramine-containing compounds and nitrosoamine-containing compounds can be mentioned. The amino-containing compounds that can be used are virtually unlimited, thus including azodicarbonamide, urea, aminoguanidine bicarbonate, biuret, dicyandiamide, hydrazides (e.g. acetohydrazide, 1,2-diacetylhydrazine, laurohydrazide, salicylohydrazide, oxalodihydrazide, carbohydrazide, adipodihydrazide, sebacodihydrazide, dodecanediohydrazide, isophthalohydrazide, methyl carbazate, semicarbazide, formhydrazide, 1,2-diformylhydrazine) and so on. The nitramine-containing compounds that can be used are also virtually unlimited and include aliphatic and alicyclic compounds containing one or more nitramine groups as substituents, such as dinitropentamethylenetetramine, trimethylenetrinitramine (RDX), tetramethylenetetranitramine (HMX) and so on. The nitroamine-containing organic compounds that can be used are also virtually unlimited and include aliphatic and alicyclic compounds containing one or more nitrosoamine groups as substituents, such as dinitrosopentamethylenetetramine (DPT). Among these nitrogen-containing compounds, azodicarbonamide has been used widely as a resin blowing agent, and being of low fire-causing potential and low toxicity and, hence, least likely to be hazardous, this compound is particularly suitable. These nitrogen-containing compounds can be used either alone or in combination. Moreover, commercially available nitrogen-containing compounds can be liberally selected from a broad range. Generally, it can be used as they are. There is no limitation on the form or grain size of the nitrogen-containing compound and a suitable one can be selectively employed.

The oxidizing agent to be used in this invention is a halogen oxo acid salt. As the halogen oxo acid salt, any of the known species can be employed. Preferred are halogenates and perhalogenates and particularly preferred are the corresponding alkali metal salts. The alkali metal halogenates include chlorates and bromates such as potassium chlorate, sodium chlorate, potassium bromate and sodium bromate, among

others. The alkali metal perhalogenates include perchlorates and perbromates such as potassium perchlorate, sodium perchlorate, potassium perbromate and sodium perbromate, among others. These halogen oxo acid salts may be used alone or in combination. The amount of the halogen oxo acid salt is generally stoichiometric, that is to say the amount necessary for complete oxidation and combustion of the nitrogen-containing compound based on its oxygen content, but since the burning velocity, combustion temperature and combustion product composition can be freely controlled by varying the ratio of halogen oxo acid salt to nitrogen-containing compound, its amount can be liberally selected from a broad range. By way of illustration, about 20 - 200 parts by weight, preferably 30 - 200 parts by weight, of the halogen oxo acid salt can be used for each 100 parts by weight of the nitrogen-containing compound. The form and grain size of the halogen oxo acid are not particularly critical and can be selected in each case.

The composition of this invention may contain, within the range not affecting its performance characteristics, at least one additive selected from the group consisting of burning control catalysts, antidetonation agents and oxygen donor compounds in addition to said two essential components.

The combustion control catalyst is a catalyst for adjusting the burning velocity, which is one of the basic performance parameters, according to conditions of the intended application, with safety parameters such as low shock ignition and non-detonation properties and other basic performance parameters such as the gas output being fully retained. Such combustion control catalyst includes, among others, the oxides, chlorides, carbonates and sulfates of Group IV or Group VI elements of the periodic table of the elements, cellulosic compounds and organic polymers. The oxides, chlorides, carbonates and sulfates of Group IV or VI elements include ZnO , ZnCO_3 , MnO_2 , FeCl_3 , CuO , Pb_3O_4 , PbO_2 , PbO , Pb_2O_3 , S , TiO_2 , V_2O_5 , CeO_2 , H_2O_3 , CaO_2 , Yb_2O_3 , $\text{Al}_2(\text{SO}_4)_3$, ZnSO_4 , MnSO_4 , FeSO_4 , etc. Among the cellulosic compounds mentioned above may be reckoned carboxymethylcellulose and its ether, hydroxymethylcellulose and so on. The organic polymers mentioned above include, among others, soluble starch, polyvinyl alcohol and its partial saponification product, and so on. These combustion control catalysts can be used alone or in combination. The amount of the combustion control catalyst is not critical and can be liberally selected from a broad range. Generally, however, this catalyst is used in a proportion of about 0.1 - 50 parts by weight, preferably about 0.2 - 10 parts by weight, based on 100 parts by weight of the nitrogen-containing compound and halogen oxo acid salt combined. The grain size of the combustion control catalyst is not critical and can be appropriately selected.

The antidetonation agent is added for preventing the detonation which may occur when the gas generating composition is involved in a fire in the course of production, handling or transportation or subjected to an extraordinary impact. As the addition of such antidetonation agent eliminates the risk of detonation, the safety of the gas-generating composition in various stages of production, handling and transportation can be further enhanced. As the antidetonation agent, a variety of known substances can be utilized. Thus, for example, oxides such as bentonite, alumina, diatomaceous earth, etc. and carbonates and bicarbonates of metals such as Na, K, Ca, Mg, Zn, Cu, Al, etc. can be mentioned. The amount of such antidetonation agent is not critical and can be liberally selected from a broad range. Generally, it can be used in a proportion of about 5 - 30 parts by weight relative to 100 parts by weight of the nitrogen-containing compound and halogen oxo acid salt combined.

The oxygen donor compound is effective in augmenting the O_2 concentration of the combustion product gas liberated from the composition of this invention. The oxygen donor compound is not critical in kind and a variety of known substances can be employed. For example, CuO_2 , K_2O_4 , etc. can be mentioned. The amount of the oxygen donor compound is not so critical and can be liberally selected. Generally, however, this donor can be used in a proportion of about 10 - 100 parts by weight based on 100 parts by weight of the nitrogen-containing compound and halogen oxo acid salt combined.

The composition of this invention may further contain, within the range not affecting its performance characteristics, a combustion temperature control agent and/or a burning velocity control agent. The combustion temperature control agent includes the carbonates and bicarbonates of metals such as Na, K, Ca, Mg, etc., among others. The burning velocity control agent includes the sulfates of Al, Zn, Mn, Fe, etc., among others. The proportion of such combustion temperature control agent and/or burning velocity control agent may generally be about 10 parts by weight, preferably about 5 parts by weight or less, based on 100 parts by weight of the nitrogen-containing compound and halogen oxo acid salt combined.

Within the range not interfering with its performance characteristics, the composition of this invention may further contain a variety of additives which are commonly used in the conventional air bag gas generating compositions.

The composition of this invention can be manufactured by blending the above-mentioned components. While the resulting mixture as such can be used as the gas generating composition, it may be provided in the form of a molded composition. Such a molded composition can be manufactured by the conventional

procedure. For example, the composition of this invention may be mixed with a binder in a suitable ratio and the mixture be molded. The binder may be any binder that is routinely employed. The form of such molded composition is not critical. Thus, it may be a pellet, disk, ball, bar, hollow cylinder, confetti or tetrapod, for instance. It may be solid or porous (e.g. honeycomb-shaped). It is also possible to process each component into a discrete preparation and mix them in use.

The composition of this invention has the following advantages.

(a) The composition of this invention is remarkably low in toxicity and the potential to cause a fire on decomposition or combustion. Therefore, the risk of hazards in handling in the course of production is very low. It can be easily molded, too.

(b) The composition of this invention has a low shock sensitivity which is either equivalent to or lower than that of the sodium azide-based gas generating composition and is, therefore, is very safe.

(c) The composition of this invention is equivalent or superior to the sodium azide-based gas generating composition in burning velocity and gas output.

(d) Like the sodium azide-based gas generating composition, the composition of this invention has a relatively low combustion temperature so that it does not have the risk of causing a burn to the passenger or a perforation or burning of the bag. In addition, the level of toxic substances in the product gas is very low.

(e) Since the base nitrogen-containing compound of the composition of this invention is not hygroscopic, it is not necessary to provide for the prevention of moisture absorption.

(f) The composition of this invention can be produced at remarkably reduced cost.

(g) Compared with the prior art gas generating compositions, the composition of this invention can be easily disposed of.

Best Mode of Practicing the Invention

The following examples are intended to describe this invention in further detail. The chemical names of the compounds indicated by abbreviations or chemical formulas in the examples are as follows.

ADCA: azodicarbonamide
DPT : dinitrosopentamethylenetetramine
RDX : trimethylenetrinitramine
HMX : tetramethylene tetranitramine
NQ : nitroguanidine

Example 1

The nitrogen-containing compound and halogen oxo acid salt, with or without a combustion control catalyst, were blended according to the formulas shown below in Table 1 to provide compositions (No. 1 - No. 17) of this invention.

Table 1

No.	Gas generating base	Amount (wt %)	Halogen oxo acid salt	Amount	Combustion control catalyst	Amount
1	ADCA	45	KClO ₄	55	CuO	10
2	ADCA	35	KClO ₄	21	CaO ₂	440
3	Urea	37	KClO ₄	63	CuO	10
4	Urea	30	KClO ₄	36	CaO ₂	34
5	Hexamethylenetetramine	18	KClO ₄	82	CuO	10
6	Guanidine bicarbonate	56	KClO ₄	44	CuO	10
7	Biuret	40	KClO ₄	60	CuO	10
8	ADCA	42	KClO ₄	50	CaO ₂	10
9	ADCA	40	KClO ₄	40	CaO ₂	20
10	ADCA	37	KClO ₄	30	CaO ₂	30
11	ADCA	30	KClO ₄	10	CaO ₂	60
12	ADCA	41	KNO ₃	59	-	-
13	ADCA (30% ZnO)	47	KNO ₃	53	-	-
14	Cyanoguanidine	29	KClO ₄	71	CuO	10
15	ADCA	45	KClO ₄	55	CuO	10
16	Oxalodihydrazide	40	KClO ₄	60	CaO ₂	3
17	Carbohydrazide	39	KClO ₄	61	CuO	10

ADCA (30% ZnO): an ADCA-ZnO mixture containing 30 wt. % of ZnO

Using a hydraulic tablet machine, each of the above compositions of this invention was compressed at 60 kg/cm² to prepare pellets (5 mm in diameter and 5.0 mm high) and each pellet sample was subjected to the 7.5-liter bomb test. The results are shown in Table 2.

[Bomb (or Vessel) test]

The procedure of the bomb test is now described with reference to Figs. 1 - 3.

1. Weigh out a predetermined amount of the sample (gas generating composition (9), pellets of compositions Nos. 1 - 15 of this invention) to place it into a chamber (1).

The chamber is provided in two sizes. The larger chamber measures 50 mm in inside diameter and 50 mm high (Fig. 2) and the smaller chamber measures 30 mm in inside diameter and 50 mm high (Fig. 3).

2. Fit up the chamber with a nozzle having a predetermined diameter (10) and an aluminum rupture plate (11) (0.2 mm thick).

3. Set an ignitor (12) in the reaction chamber. The ignitor comprises a Saran® wrap containing a mixture (2:8) of 0.3 or 1.0 g of boron and KNO_3 and a Ni-Cr wire coil (13) (0.3 mm dia. x 100 mm long) passed through the wrap.

4. Cover the chamber and connect it to a gas trapping bomb (2).

5. Connect ignition leads (4) to electrodes (5) on the bomb cover.

6. Fix the bomb cover (3) on the bomb (2).

7. Connect the measuring circuit wiring.

8. After counting down, energize the ignitor and record the chamber and bomb time-pressure curves and bomb internal temperature.

Table 2

No.	Amount (g)	Igniter (g)	Chamber L/S Nozzle diameter	CP _{max} (kgf/cm ²)	W _{1/2} (msec)	BP _{max} (kgf/cm ²)	T ₉₀ (msec)	BT _{max} (°C)
1	5	0.3	S	6 mm	>140	7.5	-	400
	5	1.0	L	4 mm	140	4.7	34	150
	2	0.3	S	6 mm	46	0.7	10	72
	2	1.0	S	6 mm	140	4.4	8	280
	5	1.0	L	6 mm	100	4.8	28	225
	5	1.0	L	4 mm	149	4.6	26	249
2	5	1.0	L	4 mm	ca. 134	3.4	-	176
3	5	1.0	L	4 mm	65	3.5	66	176
5	5	1.0	L	4 mm	74	4.8	84	366
6	5	1.0	L	4 mm	82	2.4	38	128
7	5	1.0	L	4 mm	54	2.3	49	147
8	5	1.0	L	6 mm	54	4.7	51	192
12	5	1.0	L	4 mm	50	1.4	25	-
13	5	1.0	L	4 mm	65	1.6	20	76
	5	1.0	S	6 mm	79	1.8	3	106
14	5	1.0	L	4 mm	140	5.6	18	264
15	5	1.0	L	4 mm	90	4.2	50	243
16	5	1.0	L	8 mm	120	6.0	10	-
17	5	1.0	L	9 mm	70	6.0	15	-

L: Large; S: Small

In Table 2, CP_{max} represents the maximum pressure (kg/cm²) in the reaction chamber, W_{1/2} represents the time (msec) in which the internal pressure of the chamber travels 1/2 of the maximum pressure, BP_{max} represents the maximum pressure (kg/cm²) within the bomb, T₉₀ represents the time (msec) in which the internal pressure of the bomb reaches 90% of the maximum pressure, and BT_{max} represents the maximum temperature (°C) within the bomb. Among these parameters, T₉₀ is a value simulating the inflation time of the air bag. CP_{max} is an index, the values of which indicate that the compositions of this invention retain a satisfactory performance as gas generating compositions. W_{1/2} is a parameter simulating the burning velocity of the gas generating composition within the chamber. BP_{max} is a parameter indicating the gas generating capacity per unit mass of the gas generating composition. BT_{max} is a parameter simulating the temperature of the gas in the fully inflated air bag.

Example 2

The nitrogen-containing compound and halogen oxo acid salt, with or without the combustion control catalyst, were blended according to the formulas (wt. %) shown below in Table 3 to provide compositions of this invention.

Each of the compositions of this invention was subjected to the following shock ignitability (sensitivity) test. As controls, the prior art gas generating compositions ($\text{NaN}_3\text{-KClO}_4\text{-Fe}_3\text{O}_4$ and $\text{NaN}_3\text{-CuO}$) were also subjected to the shock ignitability test.

[Shock ignitability test]

This test is designed to measure the degree of readiness of gas generating compositions to be ignited by a shock (shock ignition sensitivity). The experimental procedure is now described with reference to Figs. 4 - 7.

1. [Fig. 4]

Weigh 5 g of the sample powder (16) into a stainless steel test vessel (15). The vessel (15) is a bottomed cylinder made of stainless steel (SUS 304) and measuring 31 mm in inner diameter, 36 mm in outer diameter, 2.5 mm thick and 55 mm high.

2. [Fig. 5]

Place polyethylene cards (17) of required thickness on the sample. The sum of the thicknesses of these polyethylene cards (17) is called the gap length.

3. [Fig. 6]

Drill a hole, 6.5 mm in diameter, through two 1 mm-thick polyethylene cards (18), set a detonator (19) in the hole and set the assembly in a stainless steel vessel (15). The detonator used was Nippon Kayaku electric detonator No. 0.

4. [Fig. 7]

For testing any gas generating composition containing a hygroscopic gas generating base (e.g. sodium aside), cover the stainless steel vessel (15) with paraffin (20) for preventing the absorption of moisture.

5. Set this stainless steel vessel securely in a vice in an explosion dome and energize to fire the detonator.

6. Observe whether the sample is ignited or not.

7. [Fig. 8]

If no ignition takes place at the gap length of 1 mm, set 20 g of sample powder (16), insert the detonator D (19) into the sample, place a threaded lid (21) on the stainless steel vessel (15), and perform the test. By this procedure, even a material with a very low shock sensitivity can be ignited or exploded.

Table 3 shows the ignition limit gap length (ignitable up to that gap length) and the non-ignition limit gap length (not ignitable beyond that gap length).

In this test, a greater critical gap length value represents a higher shock ignition sensitivity. In other words, the greater the critical ignition gap length, the higher is the shock ignition sensitivity and, hence, the risk of hazards.

Table 3

No.	Gas generating base	Amount (wt %)	Halogen oxo acid salt	Amount (wt %)	Combustion control catalyst	Amount (wt. %)	Gap length(mm) Ignition Non- ignition
1	DPT	29	KClO ₄	71	-	-	3 4
2	DPT	29	KClO ₄	71	CuO	10	4 5
3	RDX	68	KClO ₄	32	-	-	4 5
4	RDX	68	KClO ₄	32	CuO	10	3 4
5	HMX	68	KClO ₄	32	-	-	4 5
6	HMX	68	KClO ₄	32	CuO	10	5 6
7	NQ	60	KClO ₄	40	-	-	4 5
8	RDX	61	NH ₄ ClO ₄	39	-	-	3 4
9	HMX	61	NH ₄ ClO ₄	39	-	-	8 10
10	RDX	65	KNO ₃	35	-	-	2 3
11	HMX	65	KNO ₃	35	-	-	2 3
12	RDX	48	NH ₄ NO ₃	52	-	-	2 3
13	HMX	48	NH ₄ NO ₃	52	-	-	2 3
14	ADCA	42	KClO ₄	58	ZnO	4.7	32 34
15	ADCA	45	KClO ₄	55	ZnO	5	25 32
16	ADCA	45	KClO ₄	55	ZnO	-	6 8

Table 3 (continued)

No.	Gas generating base	Amount (wt %)	Halogen oxo acid salt	Amount (wt %)	Combustion control catalyst	Amount (wt. %)	Gap length(mm) Ignition Non- ignition
17	ADCA	30	NaBrO ₃	70	-	-	40 64
18	ADCA	45	KClO ₄	55	-	-	with lid, insertion 1
19	ADCA	45	KClO ₄	55	CuO	10	1 2
20	ADCA	45	KClO ₄	55	Pb ₂ O ₄	10	1 2
21	ADCA	45	KClO ₄	55	CuO	1	with lid, insertion 1
22	ADCA	70	KClO ₄	30	CuO	100	with lid, insertion 1
Control A	NaN ₃	60	KClO ₄	10	Fe ₃ O ₄	30	36 37
Control B	NaN ₃	40	CuO	60	-	-	4 5

It is clear from Table 3 that the shock sensitivity of the composition of this invention is equal to or lower than that of the prior art composition, thus being as safe as or safer than the latter.

Example 3

Azodicarbonamide (abbreviated as ADCA in the following table) and a halogen oxo acid salt, with or without a combustion control catalyst, were blended according to the formulas (wt. %) shown in Table 4 to provide compositions of this invention.

Using a hydraulic tablet machine, each of these compositions was compressed at 60 kg/cm² to prepare pellets (7.6 mm in diameter, 3 mm high) and the pellet sample was subjected to the 7.5-liter bomb test described hereinbefore. The results are shown in Table 4.

As a control, the prior art gas generating composition (NaN₃-CuO) was also subjected to the 7.5-liter bomb test. The results are similarly shown in Table 4.

In this 7.5-liter bomb test, two 0.1 mm - thick aluminum plates were used as the rupture plate to be attached to the chamber cover.

Table 4

No.	Gas generating base	Amount (wt %)	Halogen oxo acid salt	Amount (wt %)	Combustion control catalyst	Amount (wt %)	Chamber		BP _{max} (kgf/cm ²)	T ₉₀ (msec)
							L/S	Nozzle dia.		
1	ADCA	45	KClO ₃	55	CuO Soluble starch	10 2.2	L	12 mm	7.0	25
2	ADCA	45	KClO ₃	55	CuO Soluble starch	10 1.1	L	8 mm	7.6	29
3	ADCA	45	KClO ₃	55	CuO	1	S	11 mm	4.2	24
4	ADCA	50	KClO ₃	50	-	-	S	11 mm	4.1	20
5	ADCA	70	KClO ₃	30	-	-	S	7 mm	7.2	26
Control NaN ₃		60	-	-	CuO	40	S	9 mm	3.8	25

L: Large; S: Small

Example 4

An air bag inflator reactor was loaded with 20 g of pellets (12.3 mm dia. x 3 mm thick) of the composition of this invention comprising 45 parts by weight of azodicarbonamide, 55 parts by weight of sodium chlorate and 2.75 parts by weight of MnO₂ and the loaded inflator was connected to a 28.6-liter tank

equipped with a pressure sensor. Using 1 g of B-KNO₃, the pellets were ignited for combustion. The maximum pressure within the tank was 4.3 kgf/cm² gauge and the tank internal pressure rise time associated with combustion of this composition was 50 msec.

As a control, 20 g of pellets (12.3 mm dia. x 3 mm thick) of the gas generating composition suggested by Japanese Examined Patent Publication No. 21171/74, i.e. a composition comprising 200 parts by weight of azodicarbonamide, 90 parts by weight of sodium chlorate and 10 parts by weight of aluminum, were also subjected to the same tank test. As a result, the rapid combustion of the ignitor alone was observed and the gas generating composition was not as efficiently combusted. Moreover, the maximum ultimate pressure in the tank was as low as 0.3 kgf/cm² gauge.

Example 5 and 6

Two-hundred (200) parts by weight of azodicarbonamide (abbreviated as ADCA in the following table) was blended with 90 parts by weight of sodium chlorate to provide a composition of this invention.

A control gas generating composition was prepared according to the suggestion made in Japanese Examined Patent Publication No. 21171/74. Thus, 200 parts by weight of azodicarbonamide was blended with 90 parts by weight of sodium chlorate and 10 parts by weight of Zr powder to provide a control composition.

Each of the above compositions was molded into pellets (5 mm in diameter x 5.0 mm high) in the same manner as Example 1 and the pellet samples were subjected to the following nozzle-pipe combustion test and the shock ignitability test. The results are shown in Tables 5 and 6.

[Nozzle-pipe combustion test]

1. Place 5 g of the gas generating composition in a flame-resistant steel vessel (a hollow cylinder measuring 50 mm in inside diameter and 50 mm high), set a Ni-Cr wire and cover the vessel. The cover is formed with an opening 7 mm in diameter.
2. Apply a voltage of 10 V across the Ni-Cr wire through a Slidac to ignite the gas generating composition.
3. Initially a white smoke emerges from the opening and, then, the composition becomes fired. The flame retention time (combustion time) from the ignition to extinguishment of the flame is visually monitored and, at the same time, recorded with a video camera.

Table 5

Gas generat- ing base	Amount (wt %)	Halogen oxo acid salt	Amount (wt %)	Combustion control catalyst	Amount (wt %)	Gap length(mm)		Combustion time (sec.)	Occurrence of a fire
						Igni-	Non-		
						tion	ignition		
Example 6	ADCA	200	NaClO_3	90	-	6	8	18	NO
Control	ADCA	200	NaClO_3	90	Zr	12	16	14	YES

Table 6

Gas generat- ing base	Amount (wt %)	Halogen oxo acid salt	Amount (wt %)	Combustion control catalyst	Amount (wt %)	Combustion time (sec.)	Occurrence of a fire
Example 7	ADCA	200	NaClO_3	90	-	15	NO
Control	ADCA	200	NaClO_3	90	Zr	10	YES (under certain conditions)

It is apparent from Table 5 that the addition of a reducing metal such as Zr increases the risk potential of a gas generating composition. While the reaction (combustion) of the composition of this invention occurs at low temperature without production of a flame, the Zr-containing control composition is combusted with production of a flame so that the temperature of the product of combustion (gas) is high. It is, therefore, clear that it is not recommendable to add a reducing metal, such as Zr, Al or Mg, to the composition of this

invention.

It is clear from Table 6 that the Zr-containing control composition is combusted with production of a flame so that the temperature of the reaction product (gas) is high.

5 Example 7

To investigate its combustibility, the composition of this invention was subjected to the strand burner test (cf. "Combustion characteristics of sodium azide gas generating systems", the Proceedings of the 1992 Annual Meeting of the Industrial Explosives Association, Pages 98-99).

- 10 1. First, 55 parts by weight of azodicarbonamide was blended with 55 parts by weight of sodium perchlorate and 5 parts by weight of zinc oxide to provide a composition of this invention.
 2. This composition was compression-molded into a rectangular piece (8 mm x 5 mm x 50 mm)- (pressure: 1.25 t/cm²) and the sides of this piece were coated with a silicone resin to prepare a testpiece with a restriction.
 - 15 3. The test was performed using a chimney-type strand combustion tester. For measurement, two holes (0.6 mm in diameter) were drilled in the testpiece at a spacing of about 40 mm and after passage of fuses (0.5 mm in diameter), the testpiece was rigidly set in the tester.
 4. After the temperature was set to the testing temperature (20 °C) in this condition, the testpiece was ignited with a Ni-Cr wire from above for combustion and the burning velocity (mm/sec.) was calculated
 - 20 from the difference between the fusion times of the two fuses and the distance between the holes.
 5. The above measurement was carried out under the pressures of 10, 20 and 40 kgf/cm².
- The measured burning velocities were 28.3 mm/sec. at 10 kgf/cm², 37.9 mm/sec. at 20 kgf/cm², and 46.0 mm/sec. at 40 kgf/cm².

25 Example 8

Using the composition of this invention as prepared by blending 30 parts by weight of azodicarbonamide with 70 parts by weight of sodium perchlorate, the burning velocity (mm/sec.) was measured as in Example 8. No ignition occurred at 10 kgf/cm². At 40 kgf/cm², the burning velocity was 48.3 mm/sec.

30 Example 9

An air bag inflator reactor was loaded with 40 g of pellets (12.3 mm in diameter x 3 mm thick) of the composition of this invention as obtained by blending 45 parts by weight of azodicarbonamide with 55 parts

35 by weight of potassium perchlorate and 10 parts by weight of copper oxide and this inflator was connected to a 28.6-liter tank equipped with a pressure sensor. The pellets were ignited with 1 g of B-KNO₃ for combustion of the composition of this invention. As a result, there was obtained a time-pressure curve similar to that obtained with 80 g of the prior art gas generating composition (NaN₃:KClO₄:Fe₃O₄ = 60:10:30) in a 28.6 liter tank.

40 Brief Description of the Drawings

Fig. 1 is a longitudinal section view showing the gas trapping bomb used in the bomb test. Figs. 2 and 3 are diagrammatic illustrations showing the chamber mounted in the gas trapping bomb on exaggerated

45 scale. Figs. 4-7 are diagrammatic representations of the procedure of the shock sensitivity test.

1. Chamber Reactor
2. Gas trapping bomb
3. Bomb cover
4. Leads
- 50 5. Electrodes
6. Thermocouple
7. Pressure sensor
8. Gas vent
9. Gas generating composition
- 55 10. Nozzle
11. Aluminum rupture plate
12. Ignitor
13. Ni-Cr wire

- 14. Pressure sensor
- 15. Stainless steel vessel
- 16. Sample powder
- 17. Polyethylene card
- 5 18. Polyethylene card
- 19. Detonator
- 20. Paraffin
- 21. Threaded cover

10 **Claims**

- 1. An air bag gas generating composition comprising a nitrogen-containing organic compound and a halogen oxo acid salt.
- 15 2. The gas generating composition of claim 1 wherein the halogen oxo acid salt is a halogenate and/or a perhalogenate.
- 3. The gas generating composition of claim 1 wherein the halogenate is an alkali metal halogenate.
- 20 4. The gas generating composition of claim 1 wherein the perhalogenate is an alkali metal perhalogenate.
- 5. The gas generating composition of claim 1 wherein the nitrogen-containing organic compound is at least one member selected from the group consisting of amino-containing organic compounds, nitramine-containing organic compounds and nitrosoamine-containing compounds.
- 25 6. The gas generating composition of claim 1 wherein the nitrogen-containing organic compound is azodicarbonamide.
- 30 7. The gas generating composition of claim 1 further containing at least one member selected from the group consisting of combustion control catalysts, antidetonation agents and oxygen donors in addition to said nitrogen-containing organic compound and halogen oxo acid salt.
- 35 8. The gas generating composition of claim 7 wherein the combustion control catalyst is at least one member selected from the group consisting of the oxides, chlorides and carbonates of Group IV and Group VI elements of the periodic table of the elements.
- 9. The gas generating composition of claim 7 wherein the combustion control catalyst is at least one member selected from the group consisting of cellulosic compounds and organic polymers.

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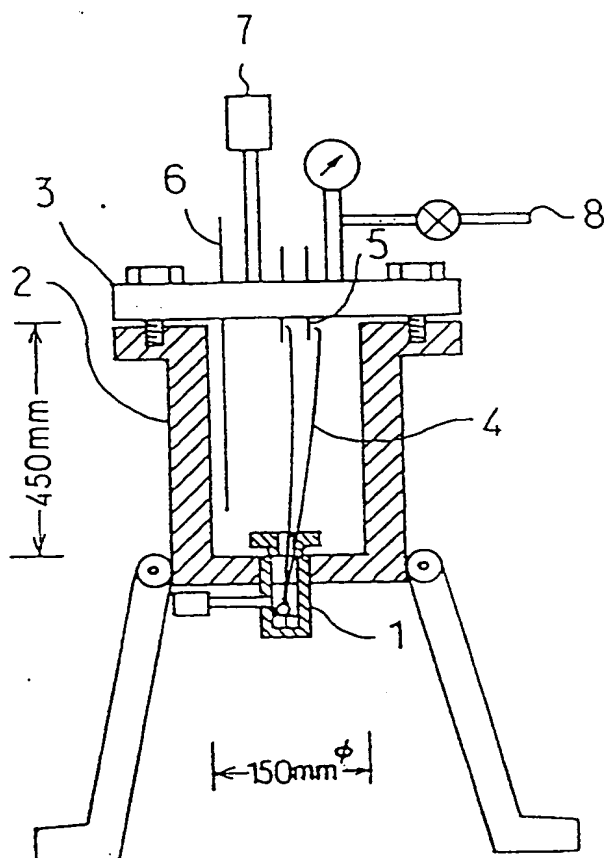
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Fig. 1



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Fig. 2

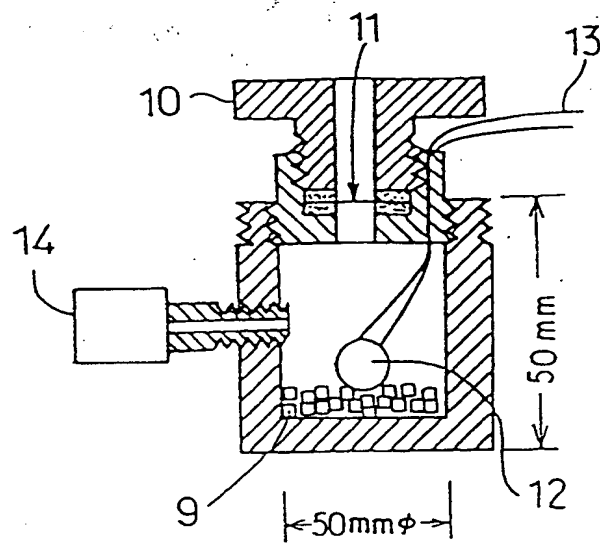
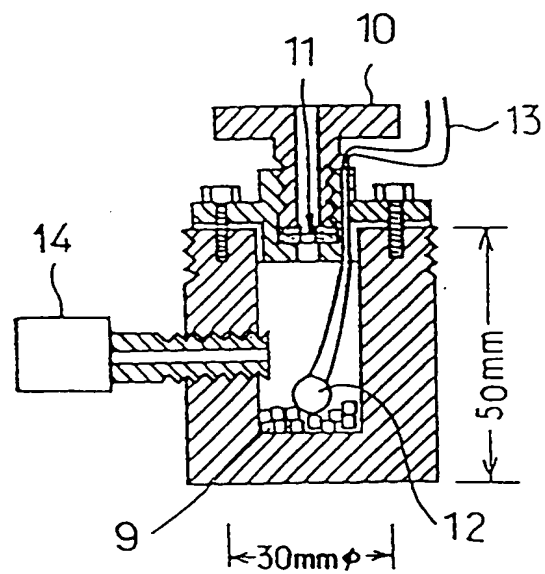


Fig. 3



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Fig. 4

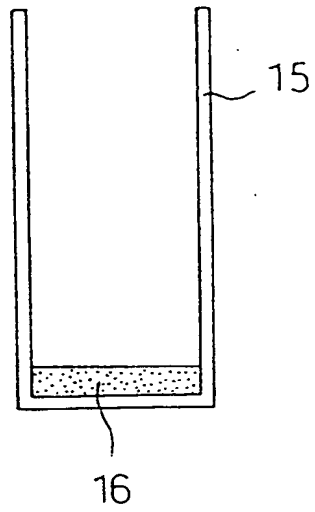
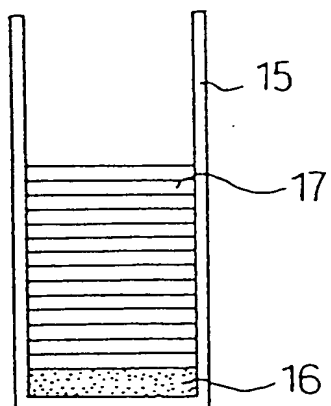


Fig. 5



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Fig. 6

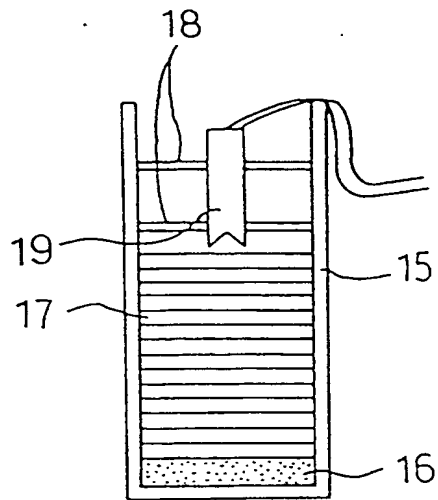
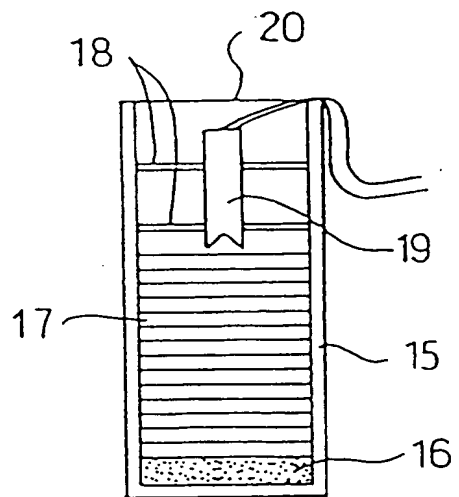


Fig. 7



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00634

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl ⁵ C06D5/00 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. Cl ⁵ C06D5/00-5/10 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, A, 2-221179 (Daicel Chemical Industries, Ltd.),	1-5
Y	September 4, 1990 (04. 09. 90),	7, 8
A	(Family: none)	6, 9
X	JP, A, 50-83270 (Nippon Oil and Fats Co., Ltd.),	1-5
Y	July 5, 1975 (05. 07. 75),	7, 8
A	(Family: none)	6, 9
PX	JP, A, 4-265292 (Automotive Systems Laboratory Inc.), September 21, 1992 (21. 09. 92), & US, A, 5035757 & EP, A1, 482852 & AU, A, 9185809 & CA, A, 2052966	1-5
X	JP, A, 2-221179 (Daicel Chemical Industries, Ltd.),	1-5
Y	September 4, 1990 (04. 09. 90),	7, 8
A	(Family: none)	6, 9
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search August 25, 1993 (25. 08. 93)		Date of mailing of the international search report September 14, 1993 (14. 09. 93)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00634

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 4-26579 (Daicel Chemical Industries, Ltd.), January 29, 1992 (29. 01. 92), (Family: none)	7, 8
A	JP, A, 3-153593 (Automotive Systems Laboratory Inc.), July 1, 1991 (01. 07. 91), & US, A, 4931111 & EP, A2, 428242 & AU, A, 9052076 & CA, A, 2012607	7-9
A	JP, B2, 60-28797 (Thiokol Corp.), July 6, 1985 (06. 07. 85), & DE, A1, 2718013 & FR, A, 2360537 & US, A, 4084992 & GB, A, 1542620	7-9